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An Investigation of the Silica Deposits of Southern Illinois

AN INVESTIGATION OF THE SILICA DEPOSITS OF SOUTHERN ILLINOIS

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY George Edward Sladek

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BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science

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INTRODUCTION.

In the southern part of Illinois, in Union and Alexander Counties, there are large silica deposits which are being worked extensively. The material obtained is roughly divided into three classes known at the mines as novaculite, silica, and gannister, all, however, being found together. At the present time the novaculite, a hard chert is used for road material, for which it has a well known reputation in the South, where it is used extensively. The white soft silica which resembles flint, is used for fillers for wood, polishing powders, paints and etc., because of its fine grained structure and pure white color. The gannister is not sold for any of these purposes, but at present is used for gas retorts, where it gives satisfactory results.

In view of the great demand for acid or silica refractories it was desirable to know the properties of these three materials, with the idea of using the novaculite and silica for such purposes, if it were profitable. Furthermore, the behavior of these materials under certain conditions might be of value regarding similar materials or other forms of silica material now used. It was for this reason that this investigation was carried out.

PART 1.

PROPERTIES DETERMINING THE USE OF MATERIALS.

Chemical Analysis:-

The chemical analysis of silica materials although not a criterion for determining the use of the material, assists in judging its qualities to some extent. Although not representative of its deformation point it gives some idea as to the conduct of the material under high temperature. The silica content should be between 96% and 98% to produce a suitable refractory. With less than this amount its refractory power is impaired and with more

than 98% the material usually shows defects in strength and permanent expansion upon heating. The presence of 1.75% to 2.5% impurities in the form of Al_2O_3 and Fe_2O_3 is necessary to produce strong brick. The addition of impurities to the raw material does not remedy this defect to any practical extent. The presence of more than that amount usually affects the refractory property of the raw material to too great an extent. The amount of alkalies should always be less than 0.5% because of their powerful fluxing action.

A typical analysis of several silica materials used for making refractories are as follows:-

Oxides	Medina Quartzite[1]	Baraboo Quartzite[1]	Alabama Quartzite[1]	Indiana Chert[2]
SiO_2	97.80	97.15	97.70	96.67
Al_2O_3	0.90	1.00	0.96	0.48
Fe_2O_3	0.85	1.05	0.80	1.59
CaO	0.10	0.10	0.05	0.07
MgO	0.15	0.25	0.30	--
Alkalies	0.40	0.10	0.31	0.21

Although the above limits are said to be those necessary for silica material for refractories, there are exceptions to the above which often exceed them and produce good brick.

Physical Properties:-[3]

The raw silica materials necessary to produce strong brick must be hard and dense and give sharp angular fragments of various sizes when crushed. Friable weak material produces a brick of similar nature after burning. Materials such as sandstones or sands are also unsuitable due to the uniformity of the grains and to their roundness. Such materials produce a weak ware. In this

[1]K. Seaver-Trans. Am. Inst. Min.Eng. Vol.53-1910 Pp.127-8.
Manufacture and Tests of Silica Brick for By Products Coke Ovens.
[2]D. Ross - B. of S. Tech. Paper 116 - P. 54 - Silica Refractories.
[3]D. Ross - B. of S. Tech. Paper 116 - P. 67

respect quartzites are preferable to the fine grained cherts because of the latter's tendency to crush down to fine grains making up its structure, unless they possess a strong cementing material holding the particles together. Microscopic examination of thin sections of suitable materials usually show tightly interlocking grains of various sizes, in which the cementing material is in sharply defined bands between the grains.[1] Fine grain cherts, however, are not necessarily condemned because of this for some produce excellent brick.

Thermal properties of Silica:-

The usual forms of silica materials found in nature are quartz, and the cryptocrystalline varieties of forms, such as chert, chalcedony and etc. Little cristobalite and tridymite are found. By proper heat treatment, however, quartz, tridymite, or cristobalite can be produced, but not the cryptocrystalline variety. The temperatures at which these inversions take place are:-

<u>In the presence of a Flux</u>[2]

Inversion	Temperature	Remarks.
a Quartz - b Quartz	575° C	Rapid and Reversible.
b Quartz - b_2 Tridymite	870°-10°C	Slow and Reversible.
b_2 Tridymite - b Cristobalite	1470°-10°C	Slow and Reversible.
a Tridymite - b_1 Tridymite	117°C	Rapid and Reversible.
b_1 Tridymite - b_2 Tridymite	163°C	Rapid and Reversible.

When no flux is present the bQuartz to b_2Tridymite inversion does not occur and as the temperature reaches 1250°C, bcristobalite forms. With tridymite and no flux, cristobalite does not form until 1570°C is reached. Chert and chalcedony change over to tridymite at a much greater speed than quartz due to

[1]D.Ross - B.of.S. Tech. Paper 116 - p. 67
[2]C.N.Fenner - Am.Jr.Sc. Vol 36 - Page 339 - Stability Relations of Silica Materials.

its finer grained structure.[1]

These various forms of silica have different specific gravities, which means that these changes in form are accompanied by volume changes. The specific gravities range as follows:-

Quartz	2.64-2.65[2]
Chert or Chalcedony	2.54-2.64
Cristobalite	2.333
Tridymite	2.270

Thus a complete inversion of quartz to tridymite would cause a true volume increase of 16.8%. This, however, is theoretical for only after prolonged heat could this state be reached. The occurrence of these inversions therefore causes trouble in the manufacture of silica brick, and often causes apparently excellent materials to be worthless for refractories. The sluggishness of some of the inversions, which permit the production of brick which at ordinary temperatures are made up of the forms of silica, stable at high temperatures, is the factor that makes silica a valuable refractory.

Rate of Inversion.

The fact that silica minerals change their form at various temperatures and that this change proceeds more rapidly and with different effects on the strength of the material in various quartzites and cherts, causes many of these to be eliminated from use for refractory purposes. The expansion (that is due to inversion) should be eliminated as far as possible in the initial burn. This necessitates that the material decreases in specific gravity considerably during the first burn and but little in subsequent burns. The table below designates[3], (A) good material, (B) fair material, and (C) poor, where the burning was done at Cone 15-16.

[1]D.Ross -B.of S. Tech. Paper 116 - Page Silica Refractories.
[2]Iddings - Rock Minerals - Page 544
[3]D.Ross - B.of S. Tech. Paper 116 - Page 5.

	A	B	C
Before Heating	2.65	2.65	2.64
After 1st Heating Cone 15-16	2.40	2.47	2.53
After 3rd Heating Cone 15-16	2.38	2.37	2.51
After 5th Heating Cone 15-16	2.38	2.37	2.43

As seen from the table, (A) practically completes its drop in specific gravity in one burn, while (C) continues to drop after five burns. A material like (C) consists usually of a pure coarse grained type and usually cracks and weakens materially during the heating. This, of course, would weaken the ware and make it unfit for use.

The effect of the addition of various agents that can be used in bonding the silica material and of others which may come in contact with the material has been studied and various results have been obtained. Ross[1] found that Tennessee Ball Clay, Al_2O_3, CaF_2, and Fe_2O_3 did not seem to increase the rate of inversion. He found, however, that the addition of NaCl and the increasing of the lime content did to a marked degree. Shale with lime had a slight effect in this direction, but shale alone did not. The possibility of employing some agent that will hasten the inversion is excellent provided it does not impair the other properties necessary in the finished ware.

Spalling in Burned Brick:-

The principal difficulty met with in apparently good silica brick is the spalling or cracking of the brick if subjected to temperature changes, This is noticeable in load tests, where the brick spall if heated too rapidly at the beginning. Some brick, however, do not spall under the same conditions that others do. According to MacDowell[2] this is due to the volume changes at 230°C to 270°C, accompanying the a to b cristobalite inversion. This is substantiated by the fact that the spalling is diminished by repeated

[1]Ross - B. of S. Tech. Paper 116 - Page 45
[2]McDowell, page 2044. -Trans.Am.Inst.Min.Eng.-1916 Silica Refractories.

burning, which decreasesthe cristobalite and increases the tridymite. This is evident from the expansion accompanying the a to bcristobalite inversion which is 3.5%, while for the tridymite inversion it is only 0.3% due to change at 130°C. Evidently an all tridymite brick would be preferable if it is to be used below 1470°C for several reasons according to MacDowell[1]:-

1. Tridymite has the least thermal or temporary expansion.
2. Tridymite has the least specific gravity of the silica minerals and cannot cause any permanent expansion below its melting point.
3. Tridymite brick can be subjected to fairly rapid temperature changes without spalling.

Chert, or chalcedony would, therefore, be more preferable for producing brick of this type due to their inverting directly to tridymite, while the quartz forms cristobalite first and tridymite only after prolonged burning.

Conclusion:-

A good silica material should analyze 96% to 98% silica with 1.75% to 2.50% impurities in the form of Al_2O_3 and Fe_2O_3. The alkali content should be below 0.5%. The material should have a fusion point above Cone 34. In the raw state it should be hard and tough, and when crushed should break down in angular fragments of various sizes. Fine grained materials are not as desirable as those with grains of various sizes, while coarsed grained ones are usually worthless. The material should not weaken or crack upon heating, and should show but little drop in specific gravity after one heating to Cone 15-16 upon subsequent heat treatment. If possible the material should show a maximum tridymite content.

[1] McDowell, Page 2044. Am.Inst.Min.Eng.-1916 - Silica Refractories.

PART 2.

The Southern Illinois Silica.

Occurrence:[1]-

The silica deposits of southern Illinois are found in Union and Alexander Counties, occurring in the Clear Creek Chert (Oriskany Division). They are in beds of almost any thickness up to 250 feet. The origin of these deposits is at present not wholly accounted for, probably being a secondary deposit. The beds occur interbedded with limestone and green and brown slate and shale. The novaculite or hard chert, comprising the greater part of the strata is at the southern part of the field. The deposit is close to the surface enabling open pit operation. The white silica occurs in thin bands too deep for open pit work. Above and below these bands occur the beds of gannister, and sometimes interbedded with the white silica. The nature of these deposits is peculiar and no satisfactory account of their formation can be found.

Description of the Materials:-

The samples of silica vary considerably in appearance. The principal constituent of the deposit, however, is a cryptocrystalline material or a chert. This was altered slightly in some manner either before or after its deposition giving two other materials.

One sample (127) the novaculite, is a typical bluish chert. Under a microscope, mixed with the mass of chert, quartz amounting to about 10% of the total volume of the pieces, was found. These inclusions were exceedingly fine grained and irregular in shape. Brown stains occurred occas ionally, which were no doubt iron contaminations. These could be seen readily with the naked eye upon the surface of the novaculite pieces. This stain occurred in the fine cracks of the pieces for the fresh surfaces of a shattered piece of the material usually showed these yellow ferruginous stains. They were not, however, abundant enough to cause the material to have a high iron content.

[1]Holbrook - Eng.Min.Jr. 103-1917 P.1136-9. Amorphous Silica Dep. of South. Ill.

An interesting feature of this material was the presence of rhombohedral inclusions having the general shape of a calcite crystal. They were, however, isotropic and were probably cavities filled with secondary silica, for with the exception of the outline of the inclusion, the material composing them was exactly like the remainder of the pieces. In this respect this material resembles the novaculite of Arkansas, for these have the general appearance of the Illinois novaculite and the inclusions of rhombic form. The fact that these inclusions were formerly calcite crystals, which were dissolved out and the cavities filled with silica is feasible, for calcite is the most soluble mineral of any of those crystallizing in that form.[1]

The second type (Samples 1021 and 128), the white silica, is a white powdery material of chalky appearance. This contained, mixed with the powdered material, pieces of novaculite. The fine material, which passed a 100 mesh sieve appeared to be almost entirely chert, and none of the inclusions noticeable in the novaculite could be found free in it. A few small quartz grains could be found. The material is exceptionally white in color.

The third type (Samples 125, 126 and 1874), the gannister, consists of novaculite covered with and mixed with a buff covered fine powder, giving the whole an appearance of corn meal. The fine material is exceedingly fine grained and each particle is of a yellow color. Quartz particles of small size were also found in the finer material. The general appearance would lead one to believe it was weathered novaculite.

Chemical Analysis:-

The following analyses are the average of two determinations for each sample, which check within the allowable limits of variation:-

[1]Report of Arkansas Geol. Survey - 1890 - Vol.3 Page 124.

Material	Sample No.	% SiO_2	% Al_2O_3	% Fe_2O_3	% TiO_2	% CaO	% MgO	Total
Novaculite	127	98.84	0.82	0.06	-	0.72	0.25	100.30
White Silica	128	98.59	0.66	0.08	-	0.67	0.17	100.28
	1021	98.47	0.85	0.12	-	0.58	0.13	100.43
Gannister	125	96.12	1.73	0.36	Trace	1.28	0.35	99.83
	1847	96.51	1.53	0.24	Trace	1.46	0.24	99.98
	126	96.15	1.52	1.52	Trace	1.48	0.20	99.58

The high silica content of the novaculite and white silica shows the purity of the materials and their similarity in chemical content, although varying considerably in physical properties. The outstanding feature, however, is the low iron and high lime content of these materials. They show chemical analyses outside the limits for silica brick materials, but this does not necessarily condemn them.

The increased impurities in the gannisters is evident, but here also the iron content is low. The alumina and lime contents for this material shows an increase of 0.7 to 1.0% over those for the other two. The increased iron content is shown in the buff color. These samples also show a trace of TiO_2 not detected in the white silica or novaculite. The analyses show a close relation, but sample 125 shows an increased iron and alumina content over the other two. This shows in the fusion tests carried on later. The analyses of the gannisters lie within the prescribed limits.

Physical Properties:-

The physical properties of the three materials varied considerably. The novaculite was hard and brittle. It splintered into various sized particles. It required, however, considerable grinding to produce finely, powdered material. The material was so hard that when crushed in the jaw crusher it caused sparks to fly and small pieces of the steel to be chipped from the jaws. These could be removed readily by a magnet in fair quantities.

The gannister, after the novaculite was crushed to smaller pieces, could be worked like a slightly plastic clay. Pieces molded up and dried possessed enough strength to permit their being handled. This was probably due to the 10% (approximately) fine material that would pass an 80 mesh sieve before grinding.

The white silica was similar to the gannister in this respect. The fine material, however, was in greater proportion amounting to about 15%. This was caked into lumps, sometimes, which could be easily broken by hand.

Of the three materials the novaculite from the standpoint of physical properties possessed the requisites of a good material for refractories. The gannister because of the large amount of novaculite would be suitable also. The silica would hardly be suitable from this point of view.

Specific Gravity:-

The specific gravities of the materials, as was expected, were very close. The samples used for chemical analyses were used for the specific gravity determinations. The samples were all ground in an agate mortar to pass a sieve made of white cloth. The picnometer method was used for these determinations. The samples were subjected to a vacuum pressure of 3 mm. and boiling at this pressure until all the air was expelled. Weighing was done, after sample, bottle and water had been cooled to room temperature. The following results are averages of two determinations which check within .01%

Material	Sample No.	Specific Gravity.
Novaculite	127	2.640
White Silica	128	2.653
	1021	2.655
Gannister	125	2.646
	1847	2.646
	126	2.650

These results show that the material is principally chert or chalcedony, (specific gravity 2.64-2.65, and quartz (specific gravity 2.65-2.66). The

impurities are not great enough to affect this property of the materials to a marked degree, and the difference between the two forms of silica is not great enough to affect the results.

Deformation Point due to Temperature:-

This property of a material is one of the most important for refractory substances and must not be confused with the melting point, which in the case of silica is much lower. The fusion point in these tests is the deformation point under heat.

These tests were carried out in a Hoskins carbon resistance furnace. The materials which were ground down in an agate mortar to pass a 60 mesh sieve, were made up into cones, using grape sugar for a bond. These were made the same size as the standard Orton cones used for high temperatures. The cones were placed in a highly siliceous fireclay cone pad and alternated with standard cones. A heating rate of approximately 400°C per hour was maintained in each test, the total time required to reach the deformation temperature being from four to six hours. A Fery radiation pyrometer was used as a check but registered about 250°C lower than the cone scale, as was the experience of F. Footit in previous work with this instrument.

Results.

Material	Sample	Fusion Point in Cones	Fusion Point °F Pyrometer.
Novaculite	127	32-33	2825°
White Silica	128	32-33	2835°
	1021	32-33	2845°
Gannister	125	29-30	2720°
	1847	30	2750°
	126	30	2765°

The variation in the fusion temperature can be traced to the impurities in in the materials. Thus the novaculite and gannister all show about the same

chemical analysis and also show the same deformation temperature in this test. The gannister, however, shows a much lower deformation temperature as would be expected due to the increased impurities in the sample. The gannister, sample 125, shows the lowest deformation temperature, which is probably due to the increased alumina and iron content, over that of samples 126, and 1847, which analyze about the same.

Trouble was encountered in several runs due to the disappearance of the test cones. In most of the tests the cones had a corroded appearance on the corners, which seemed to indicate that volatilization took place. The possibility of this was strengthened by the detection of crystalline material found on the carbon electrodes at the end of one run. This material was found in some quantity, part being clear and colorless, and part being bluish in color.

Another peculiar feature in these tests was the carbon deposits upon the standard cones. In all cases they were darkened by the carbon, which penetrated half way into the cone. The test cones of silica in each case although made up with a carbonaceous binder were the natural color of the raw material. This was noticed in the tests in which the heating was stopped before the softening point of the test cones or standard cones was reached. No suitable explanation of this could be offered.

Washing Tests:-

This test was tried with the gannister with the view of removing some of the impurities and also of determining the character of the finer particles, which were too small to distinguish under the microscope. The following method was employed.

Ten gram lots (dried at 110°C) of each sample of gannister were shaken in distilled water with 0.01% of Na_2CO_3(which was found to produce the greatest degree of defloculation), for eight hours. After this period the samples were allowed to stand for two hours and then the water decanted from the settled

material and allowed to stand for twelve hours longer. At the end of this time it was again decanted from the settled material. At the end of thirty-six hours the water from the second decantation remained turbid with practically no settling. The suspended material was made to settle out by acidifying the water with a few drops of HCL. Each residue obtained from decanting was subjected to two shakings and decantations similar to the first one. The resulting residues were washed well and dried. The test is somewhat crude but shows the possibilities well enough.

Each residue was weighed, the silica content determined,(thus giving the impurities left by difference), examined under a microscope and the first residue given another fusion test. The following are results obtained.

Sample 1847 - Gannister

Portion	Nature of Material	% in residue	% as SiO_2	% as Impurities	Fusion Point in Cones.
1st Residue	Chert	92.3%	97.4%	2.6%	31
2nd Residue	Too small to be determined	6.3%	81.4%	18.9%	
Residue Settled by addition of HCl	"	1.7%	53.2%	46.8%	

Sample 125 - Gannister

Portion	Nature of Material	% in residue	% as SiO_2	% as Impurities	Fusion Point in Cones.
1st Residue	Chert	86.3%	97.2%	2.8%	31
2nd Residue	Too small to be determined	12.5%	80.3%	19.7%	
Residue Settled by addition of HCl.	"	1.5%	60.0%	40.0%	

Sample 126 - Gannister.

Portion	Nature of Material	% in residue	% as SiO_2	% as Impurities	Fusion Point in Cones
1st Residue	Chert	87.5%	98.0%	2.0%	31-32
2nd "	Too small to be determined	10.2%	81.2%	18.7%	
Residue settled by addition of HCl.	"	2.2%	58.1%	41.9%	

The second and third residue in each case were exceedingly fine grained and yellow in color. The change in color shows the decrease in impurities by washing, which is further checked by the percent of silica in the residue. The possibility of increasing the refractory property of the gannister is evident, if this would not affect the other properties required by refractories.

Rate of Inversion:-

The rate at which a silica material (as was pointed out before), inverts from one form to another, is one of the most important features determining its quality as a refractory substance. The agents for bonding the materials, which are necessary, might be so selected as to accelerate this inversion without affecting the refractoriness materially. Such materials were chosen with others for the purpose of determining the effect of these bonding agents upon the rate of inversion of the materials.

The general method used was as follows. Each material was ground and sized so that each sample contained the same amount of the various sized particles. Portions of each sample were mixed with the various bonding agents used, water added, and were then molded into test pieces. Sets of trial pieces containing two trials for each sample and binder were burned to different temperatures. The complete series contained, therefore, two trial pieces for each sample and binder and for each temperature burned to. Cones were employed for measuring the temperature with a pyrometer to check. The apparent specific gravities of each trial piece were determined by determining the loss of weight when suspended in water. The results obtained were plotted against temperature, giving curves for each sample and binder, showing the effect of temperature on the specific gravity. A comparison of the curves for each sample shows the effect of the binder upon the rate of inversion or change in specific gravity.

FIRST SERIES:-

The raw materials were crushed in a jaw crusher and then passed

thru screens and sized. Weighed amounts of the various sized materials were mixed together thoroughly in the following proportions:-

% of Material caught on Screens of				% of Material passing through a
10-mesh	20-mesh	30-mesh	40-mesh	40 mesh Screen
10%	15%	5%	5%	65%

This corresponds approximately to the medium grind used for silica brick according to MacDowell's screen analysis.[1]

Enough of each sample was weighed out to make twenty one cubes and 2% of the binder was added to each batch. Where a salt was used enough was added to correspond to 2% of the oxide. The sample and binders were mixed together thoroughly by hand and enough water was added to make the mass workable. This varied with the material, the novaculite requiring 18%, the gannister and white silica, 25%. This was due to the fact that the latter two materials contained much finer particles in the portions that passed through the 40 mesh sieve,which was the free fine grained substance in the original samples of the raw material. After the dampened material had been mixed thoroughly by hand to insure a fair degree of uniformity throughout, it was pressed and pounded into brass molds making brickettes, 4" x 1" x 1". These pieces were then cut into four one inch cubes, care being taken not to crack them in the cutting. The trial pieces were then dried in an oven and numbered.

The binders used for the first series of the test were CaO, MgO, Plaster of Paris, $CaCl_2$, and a mixture of $MgCl_2$ and $CaCl_2$ which was calculate to give an equivalent of 1% MgO and 1% CaO. The action of the binders during mixing was same, but in the dried unburned , state gave a varied result.

The lime gave the best bond, giving a hard product so that the trial pieces could be subjected to a fairly rough handling without breaking them.

The MgO gave a fair bond, resembling that of the lime without the same

[1]McDowell - Trans.Am.Inst.Min.Eng.-1916-Silica Refractories - Page 2026.

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

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degree of toughness.

The plaster of paris gave a hard, but brittle bond so that a sharp knock caused the pieces to chip and break.

The chloride bonds were excellent immediately after removing the pieces from the drier, but after a few hours in the open the brickettes disintegrated due to the deliquescent nature of the bonding agents. Furthermore, due to their solubility in water they were carried to the surface of the trial pieces, leaving the centers with little or no bond.

SECOND SERIES:-

The results from the first series after burning were so marked that a second series was made up, with a greater number and variety of bonding agents. In this series the bonding agents used were, - 2% MnO_2 and enough CaO to make the lime content of the material equal to 2%, 2% TiO_2 and enough CaO to make total lime content 2%, 2% Tennessee No.5 Ball Clay, 2% Fe_2O_3, 2% Al_2O_3 2% Cr_2O_3, and 2% Albany Slip. The ferric oxide and alumina were added by dissolving $FeCl_3$ and $AlCl_3$ in the water used for making the mixture workable. The Cr_2O_3 was added as $Cr(NO_3)_2$ in a similar manner. After thoroughly mixing the mixtures, an excess of NH_4OH was added to precipitate the metals as hydroxides which would become oxides upon drying and firing. The purpose of this was to obtain the greatest degree of distribution of the bonding agents, thereby increasing their fluxing action upon the silica. The other materials, (powdered and passed through a 100-mesh sieve) were added dry and mixed well with the raw materials before the addition of water.

The action of the ferric hydroxide and aluminum hydroxide binders in working was much different from the rest. The water containing the salts of the two metals, when added to the dry material was sufficient to make the mixture workable. Upon addition, of 15cc. of concentrated NH_4OH the mixture immediately became too stiff to be worked or molded into trial pieces. With a little pugging

or working of the mass by hand, the mixture reached a "soft mud" consistency and would flow readily, even though no water was added, after the addition of the NH_4OH. This was probably due to the gelatinous precipitates of $Fe(OH)_3$ and $Al(OH)_3$. When they first formed, they cause the mixture to become stiffer due to their colloidal character and continuous structure throughout the mass. Upon further mixing or pugging, the excess NH_4OH acted upon these to make them more fluid, as all alkalies act upon colloids. This action is similar to that of using alkalies in mixing up clay slips for casting. The probability of the NH_4OH acting upon the silica was slight because of the short time in which this occurred. With chromium nitrate, the mass was kneaded by hand very slightly, after adding the NH_4OH, thus avoiding the action of the excess alkali upon the colloidal precipitate of $Cr(OH)_3$.

The various samples with binders were then made up into trial pieces in the same manner as was used with series I. They were dried in an electric oven at 150°C and then numbered.

The action of the bonds in the green or unburned state was varied and marked. Most of them gave poor bonds, excepting the alumina with the white silica. This gave a hard tough bond that would resist scratching with the finger nail. An unburned piece stood for three days in a pan of water without slaking down, although after this test it could be broken by hand. This strong cementing action of the alumina was not noticed or apparent in the case of the other materials (novaculite and gannister) with alumina. None of the other bonding agents had any such effect upon any of the materials.

THIRD SERIES:-

A third series was made up to check the above results and to show the effect of long burning at a low temperature. In this series, the binders used were, - 2% CaO, 2% Fe_2O_3, 2% MnO_2, 2% TiO_2, 2% Ball Clay (Tenn.No.5). The bonds were added in that state and to give a bond in the unburned state enough

lime was added to each to make the CaO content total 2%. This was necessary with all the bonds excepting the first mentioned. Additional unbonded gannister and silica trial pieces were made up to determine whether the bonds had any marked effect in increasing the inversion of the raw materials.

The Burning:-

The first series was burned in a large gas pot furnace within a a double saggar. To detect any radical temperature differences, small cone pats were placed throughout the mass of trial pieces in the saggers. These were so placed that they separated every set of two trial pieces. The burning rate was checked by a pyrometer which reached into center and the bottom of the pile of trial pieces. This registered lower than the temperatures recorded by the cones, so that cones were used in measuring the actual temperatures. This was necessary because of the variation in temperature in the furnace, which amounted to two cones or about 40°C in some cases. The rate of burning was approximately 150° per hour. This rate was maintained in the burning of the first series. The temperatures to which the trial pieces were burned were Cone 1 (1150°C), Cone 4 (1210°C), Cone 7 (1270°C), Cone 10 (1330°C), Cone 13 (1390°C), and Cone 16 (1450°C). The time required to reach these temperatures was 6, 7, 8, 9, and 10 hours respectively. Due to the variation in the temperature some of the trial pieces in the Cone 1 burn were really subjected to a Cone 2 heat treatment and were recorded as having received that instead of a Cone 1 heat treatment. This was followed throughout the experiment.

The second series was burned in a small gas kiln, where more uniform temperature control could be obtained. The trial pieces were protected from the direct play of the flames by a rough muffle built of fire brick. A pyrometer was inserted into the middle of the pile of trial pieces. The rate of burning was governed by this, but the temperature or heat treatment was measured by Orton cones. Four sets of cone pats were placed in the kiln, one on each side

of the pile of trial pieces and the burn was stopped when the desired cone was down. The temperatures the trial pieces were burned to were Conel, Cone 4, Cone 6, Cone 10, Cone 13, and Cone 16. The rate was about 150°C per hour as long as this could be maintained, but above Cone 7 this rate could not be maintained. The time of burning for each trial was 6, 7, 8, 10, 14 and 24 hours. In the last burn the temperature recorded by the pyrometer was over that of Cone 13 for the last eight hours of the burn. There was no variation in the temperature or heat treatment in the individual burns, for in each case the different cone pats from the same burns showed the same cones down.

The third series was burned to Cone 12 in the gas kiln. The temperature of Cone 6 was reached in twelve hours and then an additional twelve hours was necessary to reach Cone 12, making a total time of burning equal to 24 hours. Half of these trial pieces were then reburned to Cone 16 in an oil burning load test kiln in fourteen hours, for the purpose of determining whether the specific gravity drop was completed in the first burn or not.

Specific Gravity Determination:-

That the change in specific gravity is a measure of the amount of inversion occurring in the silica material is discussed quite fully by Ross. He shows that for ordinary work this is acceptable. This method, when used for chalcedony or chert material, is more advantageous than the optical method because of the ease and rapidity of making the determinations. The chalcedony inverts to tridymite directly rather than to cristobalite first and later to tridymite as is the case of quartzites. The specific gravity, therefore, can be considered to be a direct measure of the amount of inversion.

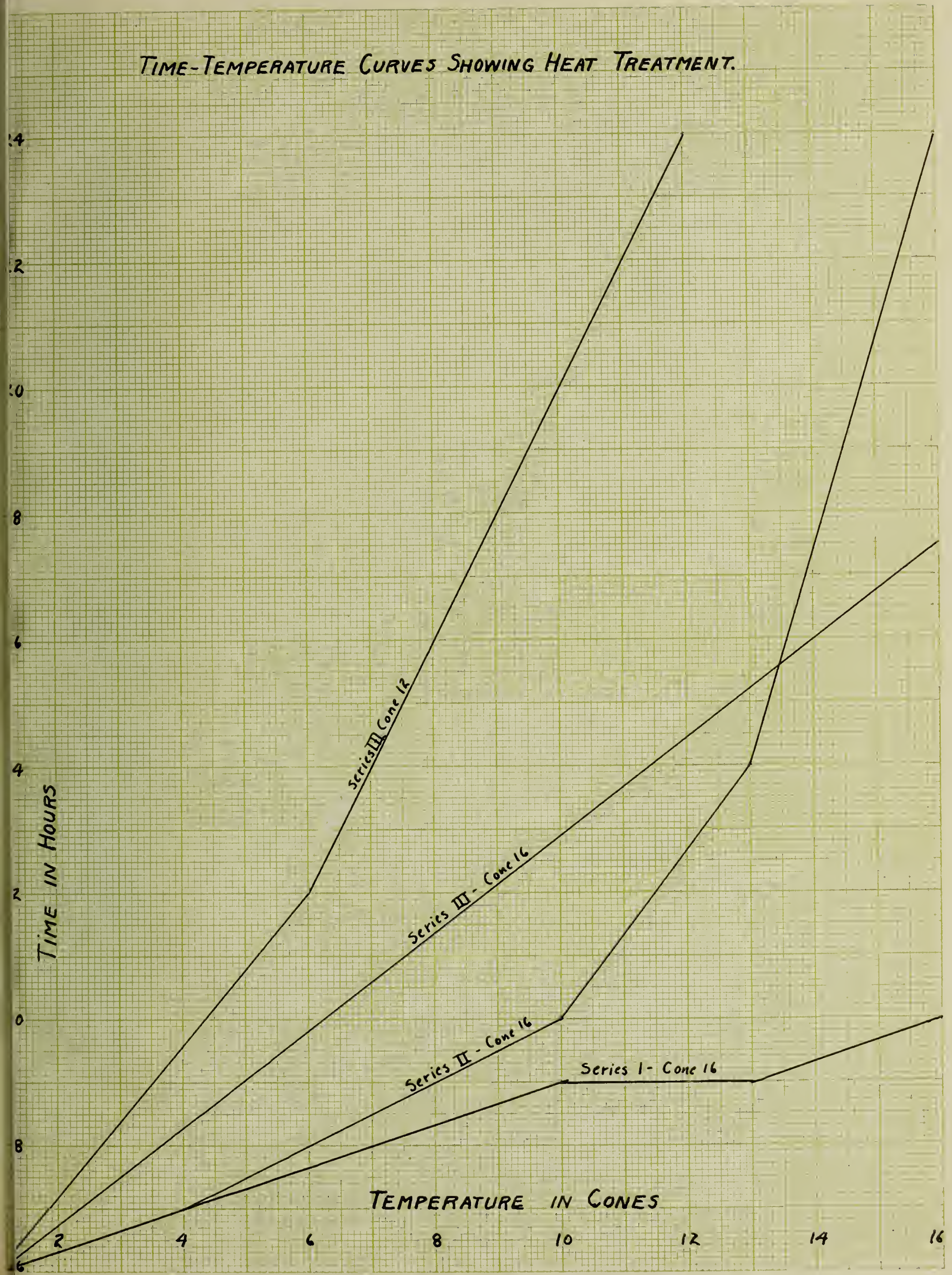
The apparent specific gravity of the trial pieces was determined in the following method. The trial pieces were saturated by subjecting them to a vacuum of 3 mm. for four hours and then boiled under a vacuum for four more hours. The saturated trial pieces were then removed and cooled to room temperature.

The weights of the trial pieces suspended in water were next determined. Then the trial pieces were dried in an electric oven at 150°C, for twelve hours, after which their dry weights were determined. The specific gravities were calculated from the dry weight divided by the dry weight minus the suspended weight, which is really the volume of the piece.

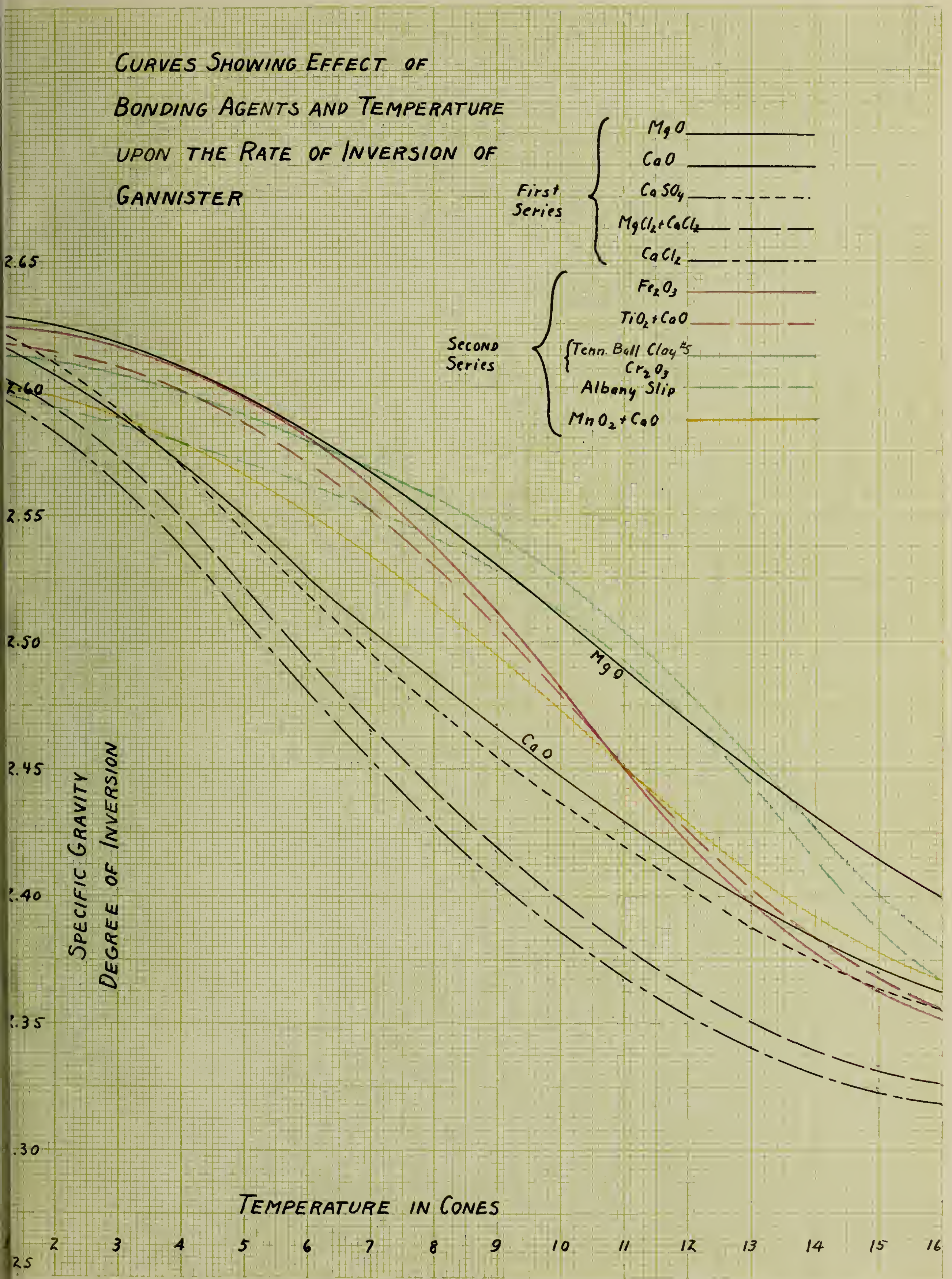
The apparent specific gravity was checked by determining the true specific by the picnometer method. These results were found to check within 0.010 which was within the limits of error of the experiment. This is consistent with the results obtained by Ross[1]. Results of check upon the specific gravity determinations are as follows:-

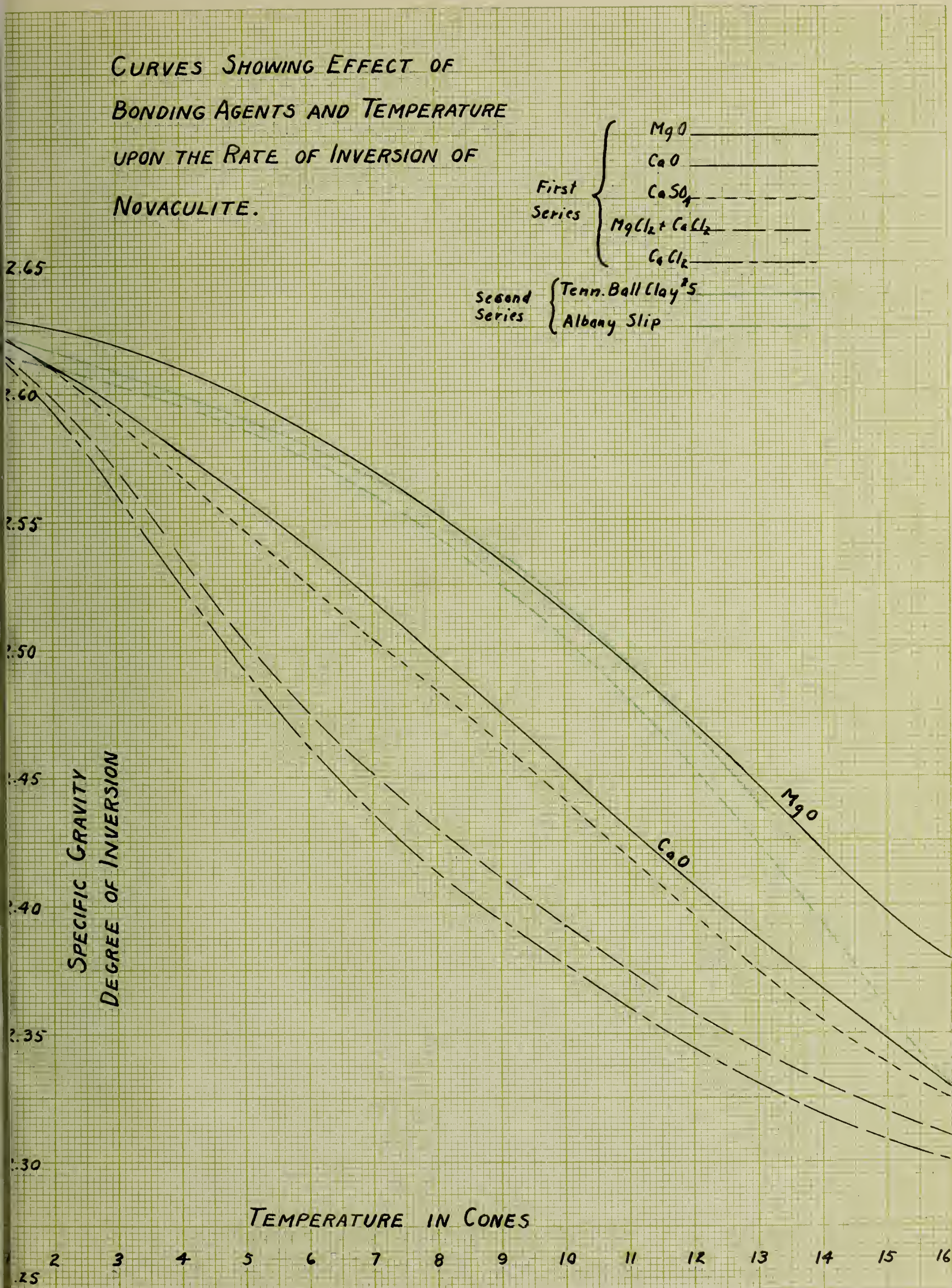
Trial Piece No.	167	168	81
True specific gravity Picnometer Method	2.308	2.300	2.335
Apparent Specific Gravity	2.310	2.310	2.340

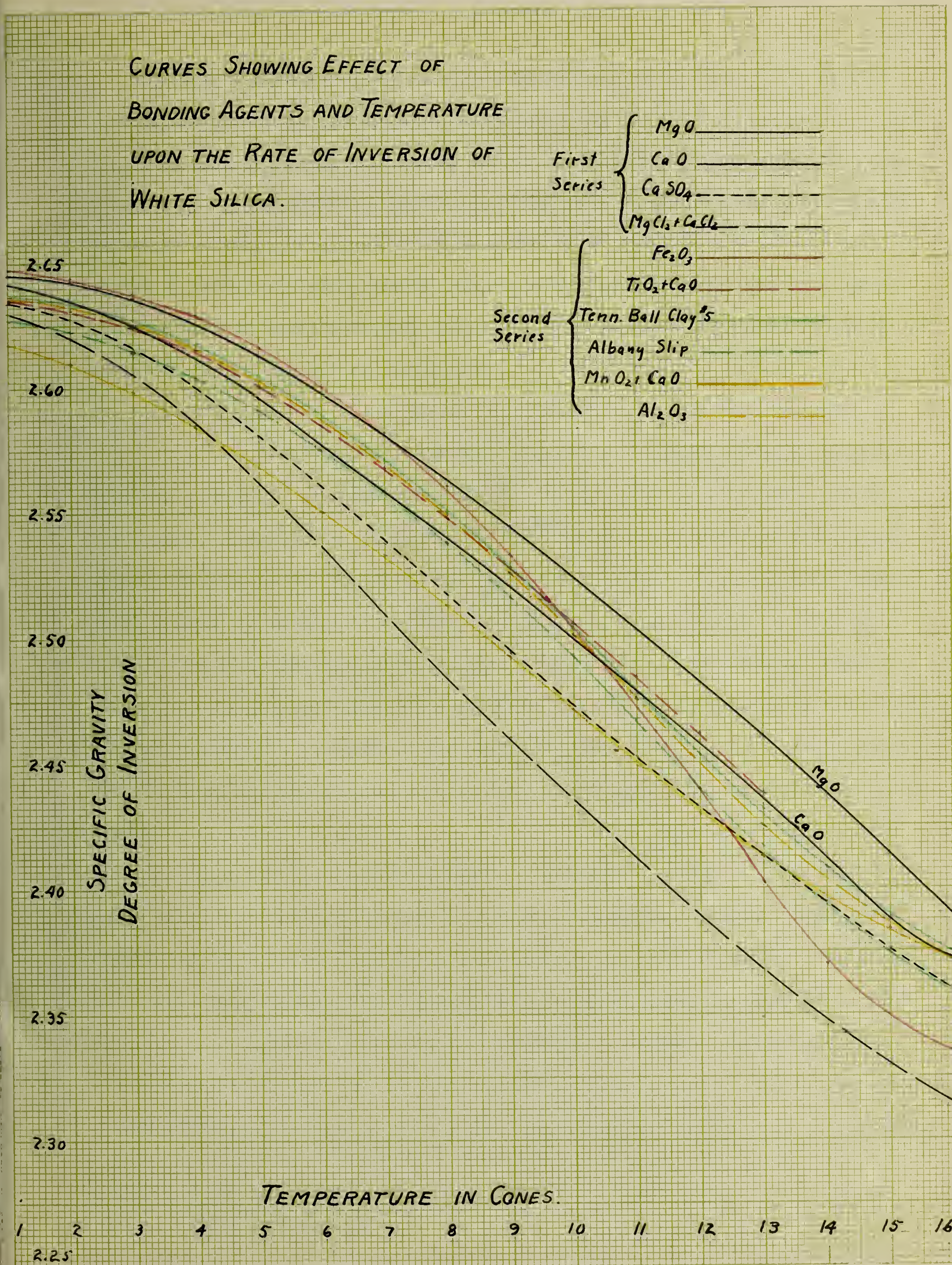
Curves were plotted from the average results obtained. These show the effect of temperature upon the rate of inversion for each binder. The curves combined as is shown on the following pages, shows the effect of the binders upon the rate of inversion. The partial curves and those lacking are due to the disintegration of the trial pieces when immersed in water and subjected to boiling in water under reduced pressure. The results used were the averages of the two trials that checked within 0.02. Those with greater variation were not used in plotting the curves.



Time-Temperature Curves Showing Heat Treatment.
Time in Hours
Temperature in Cones
Series III Cone 12
Series III - Cone 16
Series II - Cone 16
Series I - Cone 16
2
4
6
8
10
12
14
16


CURVES SHOWING EFFECT OF
BONDING AGENTS AND TEMPERATURE
UPON THE RATE OF INVERSION OF
GANNISTER
First Series
MgO
CaO
CaSO4
MgCl2+CaCl2
CaCl2
Second Series
Fe2O3
TiO2+CaO
Tenn. Ball Clay #5
Cr2O3
Albany Slip
MnO2+CaO
MgO
CaO
SPECIFIC GRAVITY
DEGREE OF INVERSION
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
2.25
TEMPERATURE IN CONES
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16


Curves Showing Effect of Bonding Agents and Temperature upon the Rate of Inversion of Novaculite.
First Series
MgO
CaO
CaSO4
MgCl2 + CaCl2
CaCl2
Second Series
Tenn. Ball Clay #5
Albany Slip
MgO
CaO
Specific Gravity
Degree of Inversion
Temperature in Cones
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
2.25
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16


CURVES SHOWING EFFECT OF
BONDING AGENTS AND TEMPERATURE
UPON THE RATE OF INVERSION OF
WHITE SILICA.
First Series
MgO
CaO
CaSO4
MgCl2 + CaCl2
Second Series
Fe2O3
TiO2 + CaO
Tenn. Ball Clay #5
Albany Slip
MnO2 + CaO
Al2O3
SPECIFIC GRAVITY
DEGREE OF INVERSION
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
2.25
TEMPERATURE IN CONES.
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
MgO
CaO

The time - temperature curves show that series 1 and series 2 are comparable to about Cone 7. Beyond this temperature the series 2 test pieces received a greater heat treatment than series 1 test pieces, due to the longer time required to reach the desired temperatures. This, of course, affects the specific gravities of the pieces, for the greater the heat treatment the greater the amount of inversion taking place. This is true for the inversions of silica from one form to another require energy.[1] Hence in comparing series 1 and 2, beyond Cone 7, this must be considered.

Series 1 :-

In the series 1 burn the results are marked. Here it is evident that $CaCl_2$ produces the greatest rate of inversion, followed by $CaCl_2$ and $MgCl_2$, $CaSO_4$, CaO and MgO, in the order named, MgO producing the least effect. This This holds true in all the three materials tested. This is true at the temperature of Cone 1, as the curves show, except in the case of $CaSO_4$ and CaO when used for bonds in the novaculite and gannister samples. In these two samples the $CaSO_4$ seems to have produced less result than lime to Cone 1. In both cases, however, above this temperature the $CaSO_4$ produces a greater rate of inversion than the lime and the curves cross at Cone 2 for novaculite and Cone 3 for gannister.

The cause for the different rates of inversion produced by these five bonds is probably due to the formation of liquids or fluxes at various temperatures. Fenner[2] in his work on "The Stability Relations of Silica Minerals", found the absence of fluxes caused the temperatures of inversion points to raised. The presence of a suitable medium for the solution and crystallization produced quicker results.[3] Ross in his work on "Silica Refractories" found an increased amount of fluxes produced a greater rate of inversion. In the case of the bonds

[1]Fenner - Previously quoted.
[2]Fenner - Previously quoted.
[3]Ross - Previously quoted.

of series 1, $CaCl_2$ melts at a temperature of 774°C[1] and acts as a flux. This is also shown with CaO and MgO. The former unites with silica forming a eutectic at 1436°C[2] and this acts as a flux, while with MgO no action takes place until a temperature of 1544°C[3] is reached. No definite data could be found on $MgCl_2$ and $CaSO_4$ in regard to melting temperatures.

The presence of gases such as Cl_2 and SO_2 might have the effect of increasing the rate of inversion. Ross found the NaCl increased the rate of inversion, but this might have been due to the fluxing action of the salt rather than to the presence of the chlorine. Fenner[4] found that milkiness in optical glass was caused by Cl and SO_3 impurities. The milkiness being due to the formation of small crystals of cristobalite, the temperature being favorable for this form. Although conditions were different from those in this experiment, the formation of cristobalite in a silicate melt tends to support the above assumption.

Series 2 :-

With all materials the Albany Slip shows a greater rate of inversion than the Ball Clay and Cr_2O_3. With all materials (novaculite trials for the remainder of the bonds disintegrated in water) the bonds for temperatures up to Cone 10 show the least effect, and TiO_2 plus CaO and MnO_2 plus CaO have a greater effect upon the rate of inversion in the order mentioned. The curves cross at this temperature and the pieces with Fe_2O_3 bond show a lower specific gravity. This is probably due to the Fe_2O_3 decomposing partially to FeO and Fe_2O_3, and FeO combining with the silica and producing a more powerful flux than the MnO_2 or TiO_2. From eutectic melting temperatures given in Spreschaal Kalendar 1916-7, $MnO \cdot SiO_2$ plus $CaO \cdot SiO_2$ as forming at 1184°C and $4FeO \cdot SiO_2$ plus $CaO \cdot SiO_2$ as melting at 1030°C. This would, however, show FeO as having a

[1]Handbook of Chemistry and Physics -The Chem. Rubber Co. Page 89
[2]Rankin and Wright -Ternary System $CaO-Al_2O_3-SiO_2$ -Am.Jr.Sc. No.39 Pp.1-80.
[3]Bowen and Anderson -Binary System $MgO-SiO_2$ Am.Jr.Sc. No.37 Pp 487-88.
[4]Fenner - Jr.Am.Cer.Soc. No.1-191 - Milkiness in Optical Glass.

greater effect at lower temperatures than MnO, but since no data can be found upon the eutectics between Fe_2O_3 and SiO_2 or MnO_2 and SiO_2 no comparison can be made from this standpoint. These three bonds, Fe_2O_3, MnO_2 plus CaO, and TiO_2 plus CaO all produce a greater rate of inversion than Al_2O_3, Ball Clay, and Cr_2O_3, as would be expected due to the comparative refractoriness of these materials mixed with silica.

In comparing the two series the Al_2O_3, Ball Clay, Cr_2O_3 and TiO_2 plus CaO bonds act similarly to the MgO bond, up to the comparable limit. The Albany Slip acts similarly to CaO, and the MnO_2 plus CaO follows the $CaSO_4$ closely in the tests upon white silica. With novaculite and gannister, the Albany Slip does not show this, but tends to act like the MgO. The results obtained in the second series, as a whole, do not show the distinct differences apparent in the first series. Because of this, no definite conclusions can be safely drawn, as can be arrived at in the first series.

Third Series:-

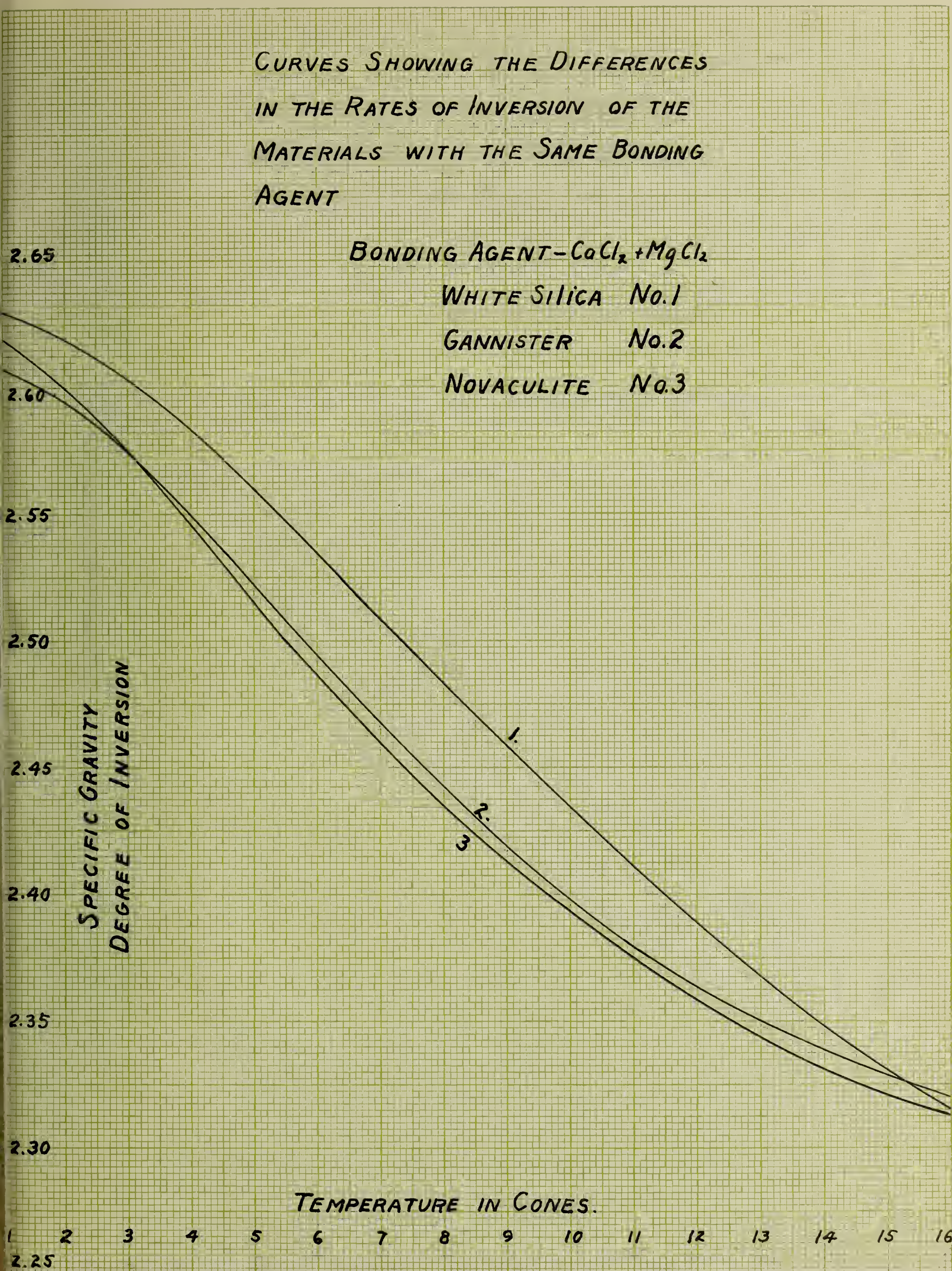
In this series it was endeavored to determine the effect of prolonged burning at a low temperature, compared to a repeated burn to a high temperature on the same trial pieces. The results show that for these materials, a twenty-four hour burn to Cone 12 is almost sufficient to produce all the inversion that could take place. It is probably that a longer burning at Cone 12 would produce the same effect as the shorter burn at Cone 16. It is evident from the table below, that the presence of fluxes increases the rate of inversion, for the gannister and white silica samples without bonds, show a higher specific gravity than those with bonds or fluxes. The three materials also show a difference in the rates of inversion. With each bond the novaculite and gannister show about the same rate, the differences not being great enough to draw any safe conclusions. The white silica, evidently, is slower in inverting than either of the other two. This is apparent from the table and the following

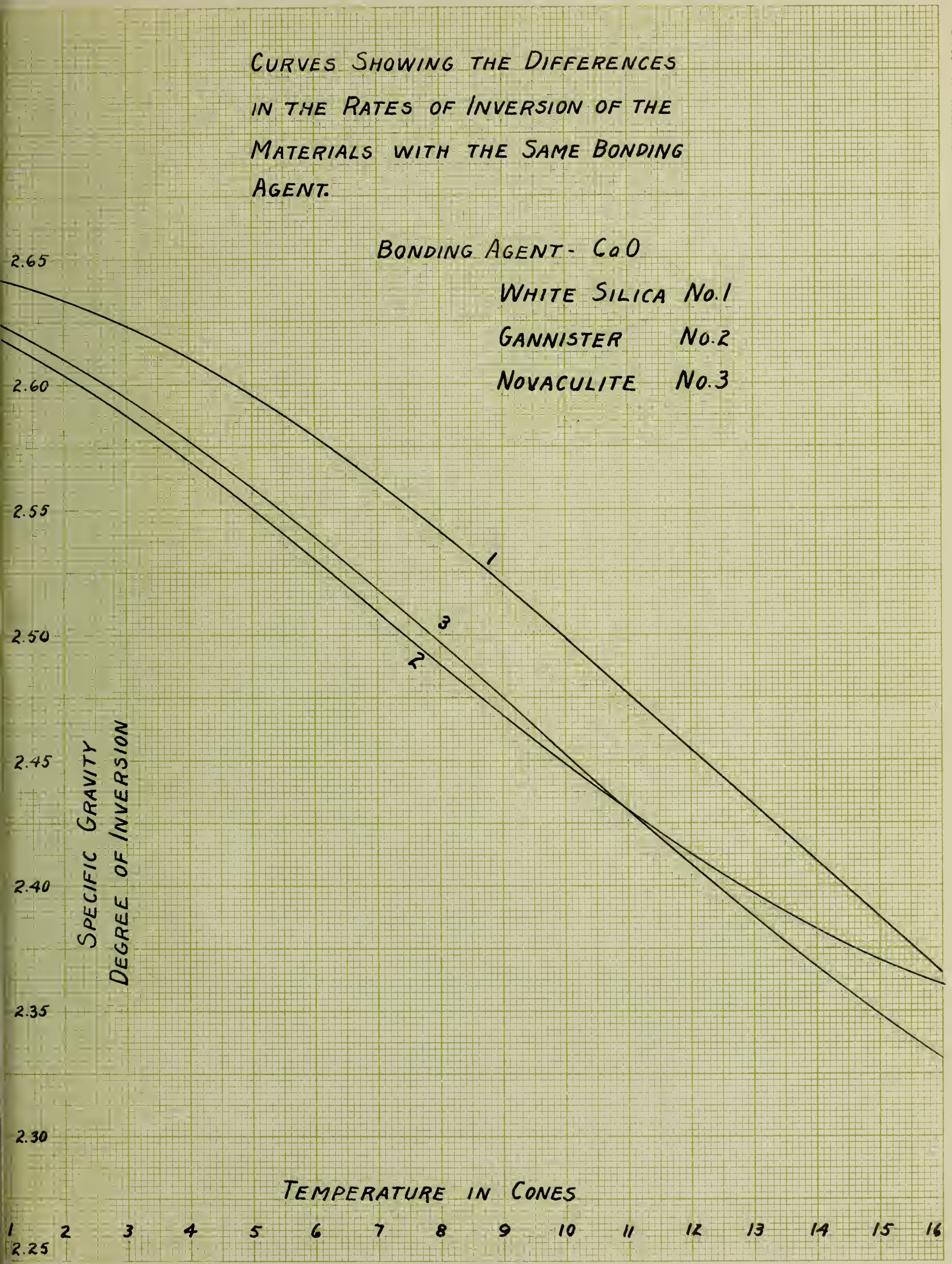
curves. The curves show these results and although they do not represent all all the bonding agents, they are sufficient in number to support the conclusions drawn below:-

Table showing Specific Gravities of Materials after

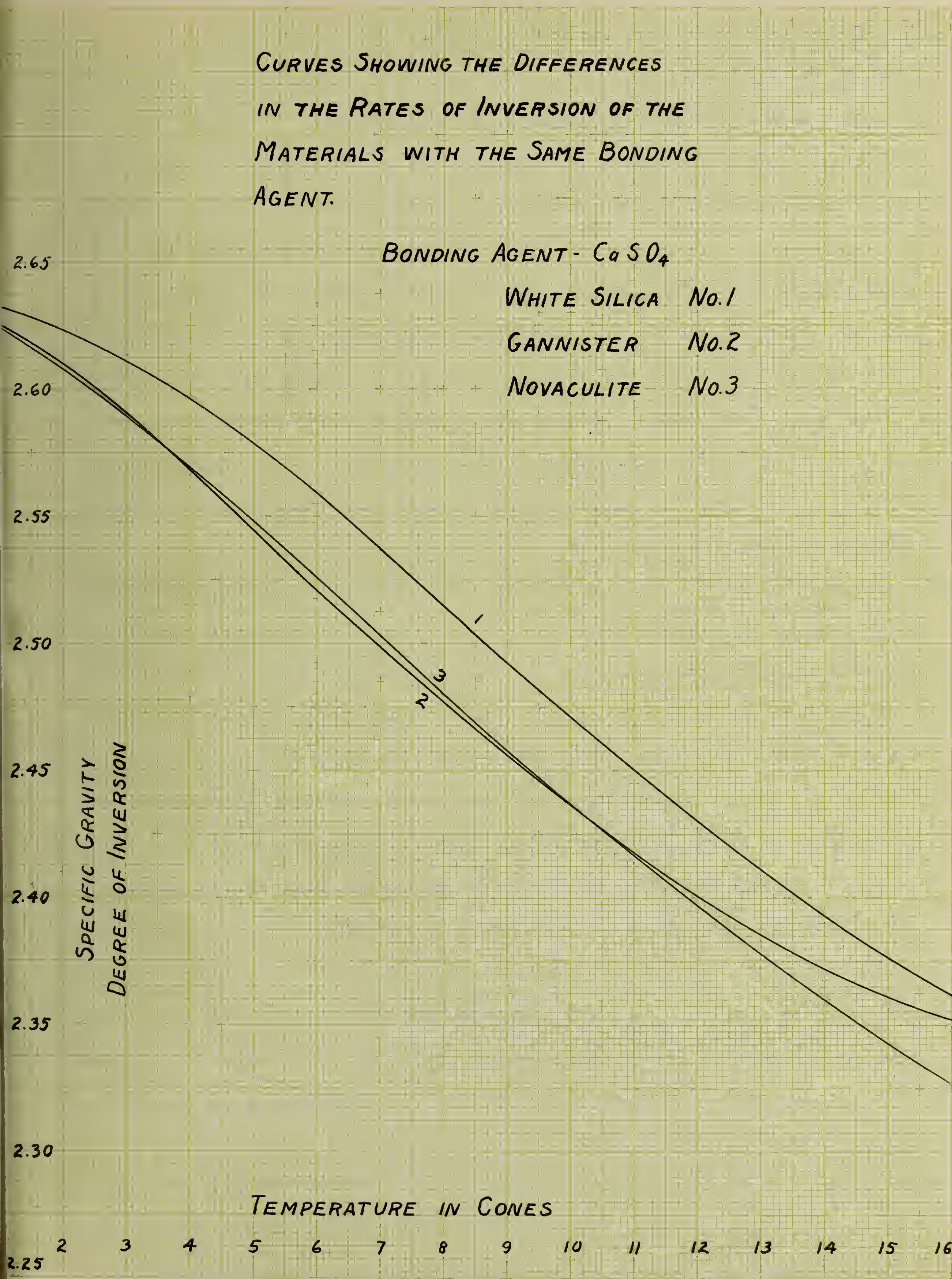
One Burn to Cone 12 and a Second Burn to Cone 16.

	Gannister		Novaculite		White Silica	
Bond	Cone 12	Cone 16	Cone 12	Cone 16	Cone 12	Cone 16
None	2.38	2.35	-	-	2.40	2.37
CaO	2.35	2.33	2.34	2.32	2.36	2.36
Fe_2O_3 plus CaO	2.34	2.32	2.34	2.32	2.36	2.36
MnO_2 plus CaO	2.34	2.32	2.35	2.34	2.36	2.38
TiO_2 plus CaO	2.35	2.33	2.36	2.33	2.38	2.35
Ball Clay plus CaO	2.35	2.33	2.36	2.36	2.37	2.35


CURVES SHOWING THE DIFFERENCES IN THE RATES OF INVERSION OF THE MATERIALS WITH THE SAME BONDING AGENT
BONDING AGENT – $CaCl_2 + MgCl_2$
WHITE SILICA No. 1
GANNISTER No. 2
NOVACULITE No. 3
SPECIFIC GRAVITY
DEGREE OF INVERSION
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
2.25
1.
2.
3
TEMPERATURE IN CONES.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16



CURVES SHOWING THE DIFFERENCES IN THE RATES OF INVERSION OF THE MATERIALS WITH THE SAME BONDING AGENT.
BONDING AGENT - CaO
WHITE SILICA No.1
GANNISTER No.2
NOVACULITE No.3
1
2
3
SPECIFIC GRAVITY
DEGREE OF INVERSION
TEMPERATURE IN CONES
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
2.25
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16


CURVES SHOWING THE DIFFERENCES IN THE RATES OF INVERSION OF THE MATERIALS WITH THE SAME BONDING AGENT.
BONDING AGENT - $CaSO_4$
WHITE SILICA No. 1
GANNISTER No. 2
NOVACULITE No. 3
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
2.25
SPECIFIC GRAVITY
DEGREE OF INVERSION
1
2
3
TEMPERATURE IN CONES
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

Comparison of the Bonds:-

The trial pieces made of gannister were always the strongest, the white silica having a tendency to be weaker and more friable. The novaculite trial pieces were all weak and friable, many of them being disintegrated in hot water in a short time.

The CaO of the bonding agents gave the best bond for all the materials but the white silica. The precipitated Al_2O_3 gave the best bond for this. The remaining bonds were inferior. The brickettes with chloride binders all burned white due to the formation of $FeCl_3$, which was then volatilized. All the pieces with such bonds had a tendency to be weak and friable.

Effect of Repeated Burning on the Specific Gravity:-

To determine the amount of volume increase (or specific gravity drop) caused by the first burn to Cone 16 in proportion to the total amount the material would undergo, some of the trial pieces were burned a third time to Cone 15. The trial pieces used for this were those of the first series with 2% CaO for a bond. These had been burned to Cone 16 in the first series test in a gas pot furnace. They were reburned in the gas pot furnace to Cone 15. The burning required twelve hours, about six hours to reach 1200°C and the remaining six to go from 1200° to 1450°C or Cone 15. The specific gravity of the pieces was determined as before, by obtaining the weight suspended in water after completely saturating the piece and then the dry weights. From this the apparent specific gravities were calculated and the averages of two determinations were taken for the result for each material. These were compared with the average results obtained from the first burning of the pieces and with the specific gravity of the raw material.

From the results shown in the following table, it is apparent that the material goes through practically the total volume change by the third burning, when CaO is used for the bonding agent. This, of course, is a desirable feature

of the materials. The strength of the white silica and gannister trials did not change apparently, but the novaculite trial pieces were more friable and very weak.

Material	Sample No.	Specific Gravity of Raw Material	Specific Gravity After 1st Burn to Cone 16	After 2nd Burn to Cone 15	After 3rd Burn to Cone 15
Novaculite	127	2.640	2.33	2.32	2.32
White Silica	128	2.653	2.36	2.32	2.31
	1021	2.651	2.35	2.33	2.32
Gannister	125	2.646	2.36	2.33	2.33
	126	2.647	2.35	2.34	2.32
	1847	2.650	2.35	2.32	2.31

The Constitution of the Pieces:-

The trial pieces from the first series of burns for the three materials, novaculite, silica, and gannister, with 2% CaO for a bond were examined under a microscope for their mineral constitution.

The probable minerals present could be quartz, chalcedony, cristobalite, tridymite and quartz glass. The differences in their indices of refraction enabled the separation of constituents to be made by using oils with indices of refraction between those of the minerals. The Becke Line method was used to determine whether substances in the samples had indices above or below that of the immersing oil.

The optical properties[1] of the minerals are as follows:-

Quartz is uniaxial with indices of refraction, E equals 1.553 and O equals 1.544. The birefringence, E minus O equals .009 is low. The mineral is colorless.

Chalcedony occurs in aggregates of radiating, and also of parallel fibers. It is colorless in thin sections and has a birefringence little lower

[1]Iddings - Rock Minerals Pp.536-543.

than that of quartz. The fibers have parallel extinction. The raw vibrating parallel to the length of the fiber is the fastest. This and the lower index distinguishes it from quartz.

Cristobalite has weak double refraction O-E equals .0005 with an index of refraction of 1.484 plus or minus .003. It is white in color.

Tridymite also has a weak double refraction amounting to about .002, but in thin sections this is so weak that it is scarcely perceptible in some cases. The average index of refraction is 1.4775, somewhat lower than that of cristobalite. This and the wedge shape nature of the twined crystals under certain conditions serve to distinguish tridymite from cristobalite.

Quartz glass is isotropic with an index of refraction of about 1.46. With the use of oils having indices of refraction equal to 1.4750, 1.4784, and 1.4998 the powdered trial pieces were examined for the various constituents. The trial pieces were all crushed in an agate mortar to pass a 200 mesh sieve. The finer particles caused trouble in the investigation but were removed so that the material used was caught on a 260 mesh sieve.

In all cases the drop in specific gravity was found to be due to the formation of tridymite from the chert. No cristobalite could be found and quartz glass, as would be, expected was absent. The approximate percentage composition from the microscope analyses followed approximately the theoretical composition of the trial pieces calculated from the specific gravity. The following results were obtained:-

Novaculite -2% CaO Bond.

Temperature	Average Specific Gr.	Observed Results % Chert	% Tridymite	Calculated Results % Chert	% Tridymite
Cone 4	2.58	93.7	7.0	84.	16.
Cone 8	2.50	70.0	30.0	62.0	38.0
Cone 10	2.45	56.0	44.0	49.0	51.0
Cone 14	2.37	31.0	69.0	27.0	73.0
Cone 16	2.33	21.0	79.0	16.0	84.0

White Silica - 2% CaO Bond.

Temperature	Average Spec. Gr.	Observed Results % Chert	Observed Results % Tridymite	Calculated Results. % Chert	Calculated Results. % Tridymite.
Cone 3	2.62	100	--	95.0	5.0
Cone 8	2.53	84.0	16.0	70.0	30.0
Cone 10	2.48	62.0	38.0	57.0	43.0
Cone 14	2.41	45.0	55.0	37.0	63.0
Cone 16	2.36	29.0	71.0	24.0	76.0

Gannister - 2% CaO Bond.

Temperature	Average Spec. Gr.	Observed Results % Chert	Observed Results % Tridymite	Calculated Results. % Chert	Calculated Results. % Tridymite.
Cone 8	2.47	66.0	34.0	57.0	43.0
Cone 10	2.45	59.0	41.0	52.0	48.0
Cone 14	2.38	34.0	66.0	30.0	70.0
Cone 16	2.36	30.0	70.0	24.0	76.0

In this work the material with an index of over that of 1.4998 was called chert, although part of it was quartz and a small amount, silicates of calcium. The results show that the specific gravity drop is due to the tridymite formation. Due to the quartz present in the material to the amount of about 10% and to the comparatively short duration of burning the lowest specific gravity value the materials could obtain in this work would be 2.31. Owing to the short heat treatment very little of the quartz inverted to cristobalite. If the quartz would invert completely to cristobalite, the minimum specific gravity would be close to 2.28. By longer heat treatment, to convert the quartz to cristobalite and then to tridymite, would only lower the specific gravity to 2.27. These conditions would never be reached for it is practically impossible to cause all the material to invert. The lower results obtained by the microscopic invest-

igation as compared with the theoretical results was partially due to the removal of the finer particles to facilitate the investigation. The crystals of tridymite were very small no doubt and the greater portion of the finer material consisted of this. The small size of these and comparative inexperience of the investigator is petrographic work did not allow him to confirm this statement by actual experiment.

Summary:-

Although these tests were not as extensive as desired, they show some interesting facts. In general, the gannister would make a suitable refractory, and is being used for retorts and similar refractories at present. Both the white silica and novaculite fail to give the strength the gannister gives and in this respect are inferior to it, although they both possess a greater refractoriness. They might, under different conditions, produce ware of requisite strength, but owing to their high silica content,(about 98.5%) it is improbable that they would. All investigations condemn materials of such a character as being unsuitable. The fusion point of the gannister can be improved by washing the raw material, but this would likely decrease its burned strength by removing some of the Fe_2O_3 and clay substance mixed with it.

In general, the rate of inversion of the materials can be accelerated by using $CaCl_2$, $MgCl_2$ plus $CaCl_2$ and $CaSO_4$ instead of CaO for bonds, but these produce a weaker piece and produce an increased porosity. The remaining oxides and materials used for bonds produced no marked result upon this property of the material. The materials as far as the rate of inversion go are superior to quartz for silica refractories because:-

1. Practically all the inversion is complete at the end of one burn to Cone 16.
2. The chert inverts to tridymite which is a desirable feature in

silica refractories for ordinary purposes.

Although this investigation shows the possibilities of these materials, considerable work remains yet to be done. The action of the materials when subjected to commercial burns, their behavior under load tests, and their spalling tendencies would offer profitable investigation. The variation of the grinding of the raw material and the method of making trial pieces might produce better ware. Before this is done none of the materials can be condemned as being valueless for refractories.

In conclusion, the writer wishes to express his indebtedness to Prof. C. W. Parmelee, for his direction and supervision of this investigation. His suggestions in the work and assistance in interpreting results were of great benefit to the writer. To Mr. E. Libman, the writer is indebted for the use of apparatus and solutions for chemical analysis and petrographic work.

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